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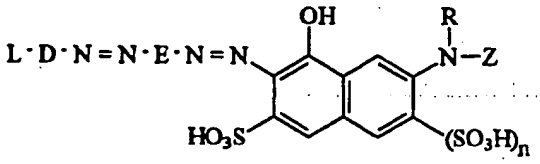

(1)

(57) Abstract

A compound of formula (1) and salts thereof, wherein: L is optionally substituted piperazinyl; D is optionally substituted phenylene or naphthylene; E is optionally substituted phenylene, naphthylene or quinolinylene; R is H or C_{1-4}-alkyl; n has a value of 0 or 1; and Z is H, alkyl or aryl free from water-solubilising groups. The compound of formula (1) is useful as a black colorant in aqueous ink jet printing inks.

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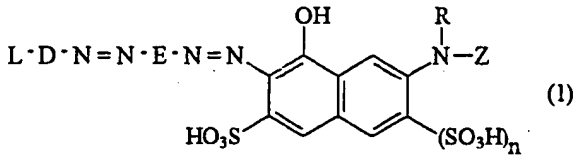
DISAZO COMPOUND

This invention relates to a disazo compound and more particularly to a colorant suitable for the preparation of an aqueous ink for use in the production of a black image by ink jet printing.

According to the present invention there is provided a compound of Formula (1) and salts thereof:



(1)

wherein:

L is optionally substituted piperazinyl;

D is optionally substituted phenylene or naphthylene;

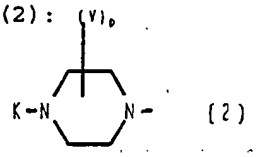
E is optionally substituted phenylene, naphthylene or quinolinylene;

R is H or C_{1-4}-alkyl;

n has a value of 0 or 1; and

Z is H, alkyl or aryl free from water-solubilising groups.

The optionally substituted piperazinyl group L is preferably of the Formula (2):



(2)

wherein:

K is H or optionally substituted alkyl, aryl, acyl or ester;

V is optionally substituted alkyl; and

p is 0, 1 or 2.

When K or V is optionally substituted alkyl, the alkyl is preferably C_{1-4}-alkyl, such as methyl, ethyl, propyl or butyl, especially methyl, each of which may be substituted as hereinafter described.

When K is optionally substituted aryl, the aryl is preferably phenyl, which may be substituted as hereinafter described.

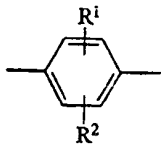
When K is optionally substituted ester, the ester is preferably of formula -COOT or SO_2OT wherein T is optionally substituted alkyl or aryl, especially C_{1-4}-alkyl or phenyl, each of which may be substituted as hereinafter described. When K is optionally substituted acyl, the acyl is preferably formyl, alkyl- or aryl-carbonyl or alkyl- or aryl-sulphonyl, in which the alkyl is preferably C_{1-4}-alkyl and the aryl is preferably phenyl, each of which may be substituted as hereinafter described. Examples of optionally

substituted piperazin-1-yl groups represented by L are piperazin-1-yl, 4-hydroxyethylpiperazin-1-yl, 4-acetyl-piperazin-1-yl, 3-methylpiperazin-1-yl, 3-methyl-4-acetyl-piperazin-1-yl, 4-formylpiperazin-1-yl and 4-methylpiperazin-1-yl.

D is preferably optionally substituted phen-1,3-ylene or phen-1,4-ylene, especially the latter.

When E is optionally substituted phenylene, the phenylene is preferably phen-1,4-ylene. When E is optionally substituted naphthylene, the naphthylene is preferably naphth-1,4-ylene. When E is optionally substituted quinolinylene, the quinolinylene is preferably quinolin-5,8-ylene, each of which may be substituted as hereinafter described.

Where E is substituted phenylene it is preferably of the Formula (2a):



(2a)

wherein

R^1 is optionally substituted alkyl, optionally substituted alkoxy or NR^3R^4;

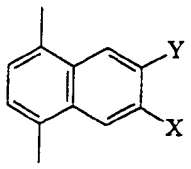
R^2 is H, halogen, -COOH, $-SO_3H$, optionally substituted alkyl, optionally substituted alkoxy or optionally substituted alkylthio;

R^3 is H or optionally substituted alkyl; and

R^4 is H, optionally substituted alkyl or acyl.

Examples of substituted phenylene groups represented by E are 2-amino-phen-1,4-ylene, 2-amino-5-methoxyphen-1,4-ylene, 2-methylamino-phen-1,4-ylene, 2-acetylaminophen-1,4-ylene, 2,5-dimethoxyphen-1,4-ylene, 2-methoxy-5-methyl-phen-1,4-ylene, 2-methylphen-1,4-ylene, 2-methoxy-phen-1,4-ylene, 2-methoxy-5-acetylaminophen-1,4-ylene.

Where E is optionally substituted naphthylene it is preferably of the Formula (2b):



(2b)

wherein each of X and Y is independently selected from -COOH, $-SO_3H$ and H. In the group of Formula (2b) it is preferred that one of X

and Y is COOH or SO_3H, especially the former and the other is H or that both X and Y are H. Examples of naphthylene groups represented by E are naphth-1,4-ylene, 6- or 7-sulphonaphth-1,4-ylene, and 6- or 7-carboxy-naphth-1,4-ylene.

By the term "water-solubilising groups" from which Z must be free, is meant acidic, hydrophilic groups which render an organic material water-soluble such as -COOH, $-SO_3H$, $-PO(OH)_2$ and $-B(OH)_2$.

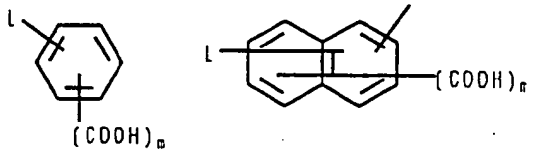
R is preferably H or methyl, but more especially H.

Z is preferably H, C_{1-4}-alkyl or phenyl, but more especially H, and, with the exception of H, these may be substituted as hereinafter defined, provided the substituent is not water-solubilising. Examples of groups represented by Z include methyl, ethyl, 2- and 4-tolyl, benzyl, methoxymethyl, methoxyethyl, ethoxyethyl, 2- and 4-anisyl, hydroxymethyl, hydroxyethyl, 4-hydroxyphenyl, 4-cyanophenyl, 4-chlorophenyl and 3-acetylaminophenyl.

Where K, V, D or E contains or represents a substituted alkyl or aryl group as hereinbefore described, each substituent on the alkyl or aryl group is preferably selected from C_{1-4}-alkyl; especially methyl or ethyl; C_{1-4}-alkoxy, especially methoxy or ethoxy; OH; CN; NO_2; -COOH; $-SO_3H$; amino; halogen, especially chloro or bromo; acylamino, especially C_{1-4}-alkylcarbonyl-amino, benzoylamino or ureido; ester, especially C_{1-4}-alkoxycarbonyl; acyl, especially C_{1-4}-alkylcarbonyl; and acyloxy, especially C_{1-4}-alkylcarbonyloxy; unless stated otherwise.

The same substituents, with the exception of -COOH and $-SO_3H$, may be present on Z.

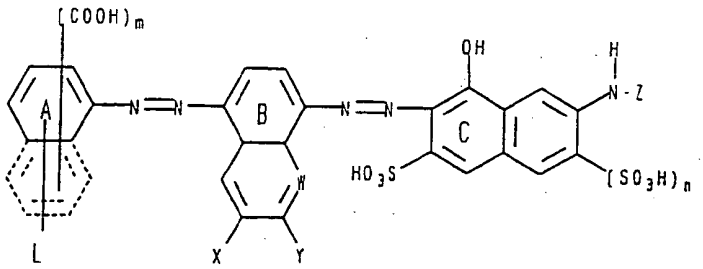
The group L-D- in Formula (1) is preferably of the Formula (3) or (4) wherein T^1 and T^2 are as hereinbefore described and m is 0 or 1.



(3) (4)

and especially of Formula (3) wherein m is 0 or 1 and L is of Formula (2) in which p is 0 or 1; V is CH_3 or OCH_3; and K is selected from H, C_{1-4}-alkyl, especially methyl; formyl; C_{1-4}-alkylcarbonyl; phenylcarbonyl; ester, especially C_{1-4}-alkoxycarbonyl or phenoxycarbonyl; and hydroxy-C_{1-4}-alkyl, especially 2-hydroxyethyl.

A further feature of the present invention provides a dye of Formula (5) and salts thereof:



(5)

wherein:

L is of Formula (2);

W is C-H, C-COOH or N;

X is H, COOH or SO_3H;

Y is H, COOH or SO_3H; and

K, V, p, m, Z and n are as hereinbefore defined provided that (1) at least one of X and Y is H or COOH and (2) W is C-H or N when X and Y are both COOH.

Nucleus A may be a phenyl or naphthyl group, preferably the former and, where it is naphthyl, the substituents shown may be on either benzene ring. Where Nucleus A is phenyl and m is 1, the COOH group is preferably in the ortho with respect to L. In formulae (3) and (5) it is preferred that m is 1.

In Nucleus B, it is preferred that W is C-H or N, especially the former. It is also preferred that one of X and Y is COOH or SO_3H, especially the former and the other is H or that both X and Y are H.

In compounds of Formula (1) and (5) it is preferred that n is 0. The compounds of Formula (1) and (5) preferably contain at least two carboxy groups. It is also preferred that the number of carboxy groups is equal to or greater than the number of sulpho groups.

Components from which Nucleus B may be derived include 1-naphthylamine, 1,6-Cleves acid, 1,7-Cleves acid, mixed Cleves acids, 8-amino-2-naphthoic acid and mixed 5-amino- and 8-amino-2-naphthoic acids. If such mixed components are employed the product will be a mixture of dyes containing different isomeric Nuclei B. Such mixtures can be made directly from mixed Cleves acids or from the mixed isomers of 5-amino-2-naphthoic acid and 8-amino-2-naphthoic acid, respectively, without the need to separate the isomers.

Components from which Nucleus C may be derived include Gamma acid, 2R acid, N-methyl-Gamma acid, N-ethyl-Gamma acid and N-phenyl-Gamma acid.

According to a further feature of the invention there is provided an intermediate of the Formula (6):

$$L\text{-}D\text{-}NH_2 \qquad (6)$$

wherein L and D are as hereinbefore defined.

Examples of intermediates of Formula (6) include 3-carboxy-4-(4'-hydroxyethylpiperazinyl)aniline, 3-carboxy-4-piperazinylaniline, 4-(4'-methylpiperazinyl)aniline, 4-[(4'-acetyl-piperazinyl)-3-carboxy-aniline, 4-[(4'-acetyl-3'-methylpiperazinyl)-3-carboxyaniline, 4-(4'-formyl-3'-methylpiperazinyl)-3-carboxyaniline, 4-(4'-ethoxy-carbonylpiperazinyl) aniline and 4-[(3'-methylpiperazinyl)-3-carboxy-aniline.

The compounds of Formula (1) and (5) can be made by analogous processes to those described in EP 356080A. For example a compound of Formula (6) may be diazotised, e.g. in water at 0-5°C using $NaNO_2$ and acid, coupled onto an amine of formula H-E-NH_2 to give a monoazo compound, the monoazo compound may then be diazotised in a similar manner and coupled onto a suitable 1-hydroxy-3-sulpho compound having an -NHZ substituent at the 7-position and optionally a sulpho group at the 6-position; wherein E, Z and the compound of Formula (6) are as hereinbefore defined. In the compound of Formula (6) in which K, in the piperazinyl group L, is H, this may be protected by conversion to acetamido. Suitable processes are substantially as described in the Examples.

The compound of Formula (6) can be prepared by reacting a piperazine, L-H, where L is as defined in Formula (2), with a compound Cl-D-NO_2, where D is as herebefore defined, in an aqueous medium at a temperature from 50-100°C, preferably from 80-95°C for up to 24 hours, preferably in the presence of an acid binding agent, such as NaOH, Na_2CO_3 or $NaHCO_3$, to give a compound L-D-NO_2 and reducing the NO_2 group, e.g. by hydrogenation. Examples of the compound Cl-D-NO_2 are 4-chloronitrobenzene, 2-chloro-5-nitro-benzoic acid, 3-nitro-4-chloro benzoic acid, 1-nitro-4-chloronaphthalene, 1-nitro-5-chloro-naphthalene and 1-nitro-4-chloro-7-carboxy naphthalene.

A compound of Formula (1) or Formula (5), hereinafter referred to as a Colorant, is notable for its strong, neutral, black shade, fastness to water and light, and good solubility in water. Compositions of the Colorant with water-miscible organic solvents, especially such compositions contained in an aqueous medium, are characterised by a low tendency to bronze when printed on paper.

The Colorant is especially useful for the preparation of an ink, especially an aqueous ink suitable for use in ink jet printing, especially thermal ink jet printing.

The Colorant is preferably a salt of a compound of Formula (1) or Formula (5), especially a salt with an alkali metal cation or

optionally substituted ammonium cation or a mixture of such cations. An especially preferred Colorant is a salt with ammonia or a substituted ammonium ion or a mixture thereof.

The substituted ammonium cation may be a quaternary ammonium cation of the formula $^{+}NQ_4$ in which each Q independently is an organic radical, or two or three Qs together with the nitrogen atom to which they are attached form a heterocyclic ring and all remaining Qs are selected from C_{1-4}-alkyl. Preferred organic radicals represented by Q are C_{1-4}-alkyl, especially methyl. Preferred heterocyclic rings formed by NQ_4 are 5 or 6 membered heterocyclic rings.

Examples of quaternary ammonium groups of formula $^{+}NQ_4$ are $N^{+}(CH_3)_4$, $N^{+}(CH_2CH_3)_4$, N-methylpyridinium, N,N-dimethylpiperidinium and N,N-dimethylmorpholinium.

Alternatively the substituted ammonium cation may be of the formula $^{+}NHT_3$ wherein each T independently is H, C_{1-4}-alkyl or hydroxy-C_{1-4}-alkyl provided at least one T is C_{1-4}-alkyl, or two or three groups represented by T together with the nitrogen atom to which they are attached form a 5 or 6 membered ring, especially a pyridine, piperidine or morpholine ring. It is preferred that the substituted ammonium cation is derived from an amine which is volatile under ambient conditions, i.e. at 20°C and atmospheric pressure.

Examples of groups of formula $^{+}NHT_3$ are $(CH_3)_3N^{+}H$, $(CH_3)_2N^{+}H_2$, $H_2N^{+}(CH_3)(CH_2CH_3)$, $CH_3N^{+}H_3$, $CH_3CH_2N^{+}H_3$, $H_2N^{+}(CH_2CH_3)_2$, $HN^{+}(CH_2CH_3)_3$, $HN^{+}(CH_2CH_2OH)_3$, $CH_3CH_2CH_2N^{+}H_3$, $(CH_3)_2CHN^{+}H_3$, pyridinium, piperidinium and morpholinium.

It is especially preferred that the Colorant is in the form of the ammonium salt or the mono- or di-methylammonium salt.

The ammonium salt form of the Colorant can be prepared by dissolving an alkali metal salt thereof in water, acidifying with a mineral acid, adjusting the solution to pH 9-9.5 with ammonia or the appropriate amine and removing alkali metal salt by dialysis.

The compounds of Formula (1) and (5) are notable for their strong, neutral, black shade, fastness to water and light, good solubility in water and mixtures thereof with water-miscible organic solvents and low tendency to bronze when printed on paper.

The compounds are especially useful for the preparation of inks, especially aqueous inks, used in ink jet printing and particularly thermal ink jet printing.

The water-fastness of the compounds on paper may be increased by printing it from an aqueous medium in the form of an ammonium or substituted ammonium salt.

According to a further feature of the present invention there is provided an ink comprising the Colorant and a liquid medium.

It is preferred that the Colorant is completely dissolved in the liquid medium to form a solution.

The ink preferably contains from 0.5% to 20%, more preferably from 0.5% to 15%, and especially from 1% to 5%, by weight, of the Colorant based on the total weight of the ink.

The liquid medium is preferably water or a mixture comprising water and one or more water-soluble organic liquid, the water and organic liquid(s) preferably being in a weight ratio from 99:1 to 50:50 and more preferably 95:5 to 60:40 and especially 95:5 to 80:20.

The water-soluble organic liquid is preferably a C_{1-4}-alkanol such as methanol, ethanol, n-propanol, isopropanol, n-butanol, s-butanol, t-butanol or i-butanol; an amide such as dimethylformamide or dimethylacetamide; a ketone or ketone alcohol such as acetone or diacetone alcohol; an ether such as tetrahydrofuran or dioxane; an oligo- or poly-C_{2-6}-alkylene glycol such as diethylene glycol, triethylene glycol, poly(ethyleneglycol) or poly(propyleneglycol) of molecular weight up to 500; an alkylene glycol or thioglycol containing a C_{2-6}-alkylene group such as ethylene glycol, propylene glycol, butylene glycol 1,4-pentylenediol or hexylene glycol; a thiodiglycol; a polyol such as glycerol or 1,2,6-hexanetriol; a C_{1-4}-alkyl ether of a C_{2-4}-alkylene glycol or oligo-C_{2-4}-alkylene glycol such as 2-methoxy-ethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)ethanol, 2-[2-(2-methoxyethoxy)ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol or 2-[2-butoxy-ethoxy]ethanol; a heterocyclic ketone or sulphone, such as 2-pyrrolidone, N-methyl-2-pyrrolidone or sulpholane; or a mixture containing two or more of the aforementioned water-soluble organic solvents.

Preferred water-soluble organic solvents are selected from 2-pyrrolidone, N-methylpyrrolidone, sulpholane, C_{2-6}-alkylene glycols and C_{1-4}-alkyl ethers of polyhydric alcohols, such as ethylene glycol, diethylene glycol, triethylene glycol or 2-methoxy-2-ethoxy-2-ethoxy ethanol; and a polyethylene glycol with a molecular weight of up to 500. A preferred specific solvent mixture is a binary or tertiary mixture of water and diethylene glycol; water and 2-pyrrolidone; water, ethylene glycol and 2-pyrrolidone; or water, ethylene glycol and N-methylpyrrolidone in weight ratios as herein described.

The water soluble organic solvent generally promotes the solubility of the dye in the aqueous medium and also the penetration of the dye into the substrate during printing. The addition of surfactants and/or biocides is also beneficial.

Examples of other suitable liquid media are given in US 4,963,189, US 4,703,113, US 4,626,284 and EP 425150A.

It is preferred that the inks of the present invention comprise one or more penetrants, such as the water-soluble organic solvents hereinbefore described, to assist permeation of the dye into a paper substrate, a kogation-reducing agent to prevent or reduce the build-up of residue (koga) on the resistor surface in thermal ink jet printers and a buffer such as sodium borate, to stabilise the pH of the ink.

The kogation-reducing agent is preferably an oxo anion, such as described in EP 425150A. The oxo-anion may be $C_2O_4^{2-}$, SO_3^{2-}, SO_4^{2-}, molybdate, or AsO_4^{3-} but is preferably a phosphate ester, or diorgano-phosphate or more especially a phosphate salt such as a dibasic phosphate (HPO_4^{2-}), a monobasic phosphate ($H_2PO_4^-$) or a polyphosphate ($P_2O_7^{4-}$). The selection of counter ion is not believed to be critical and suitable examples include alkali metals, ammonium and alkylammonium cations. The kogation-reducing agent is preferably present in the ink at a concentration from 0.001% to 15% by weight of oxo-anion based on the total ink, and more preferably from 0.01% to 1%.

A further aspect of the present invention provides a process for printing a substrate with an ink using an ink jet printer, characterised in that the ink contains a dye for Formula (1).

A suitable process for the application of an ink as hereinbefore defined comprises forming the ink into small droplets by ejection from a reservoir through a small orifice so that the droplets of ink are directed at a substrate. This process is commonly referred to as ink jet printing, and the ink jet printing processes for the present inks may be piezoelectric ink jet printing or thermal ink jet printing. In thermal ink jet printing, programmed pulses of heat are applied to the ink by means of a resistor, adjacent to the orifice during relative movement between the substrate and the reservoir.

A preferred substrate is an overhead projector slide or a cellulosic substrate, especially plain paper, which may have an acid, alkaline or neutral character. Textile materials such as cotton, viscose, jute, hemp, flax, nylon etc may also be printed with the compounds if so desired, for example using the methods described in EP 550872A.

A preferred ink for use in the process is as hereinbefore described.

According to a still further aspect of the present invention there is provided a paper or an overhead projector slide printed with the Colorant as hereinbefore defined.

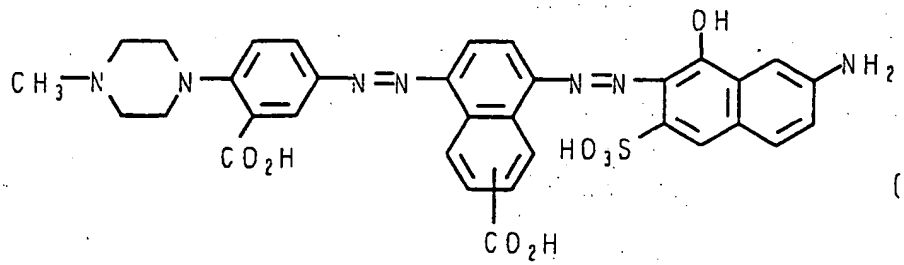
It has been found that further useful effects can be obtained if the Colorant or inks derived therefrom, as hereinbefore described, also contain a further dye or dyes of the type disclosed

for ink jet printing in EP 468647A; EP 468648A; EP 468649A and EP 559309A. Such a dye, especially the yellow dyes of EP 468647A and the cyan dyes of EP 559309A or a combination thereof, can assist in the suppression of any tendency to bronzing. The Colorant may be used in admixture with up to about 20% by weight of such dyes but more preferably from 2% to 10%, based on the weight of the resulting composition.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise indicated.

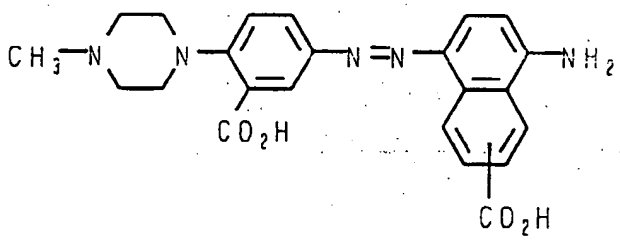
Example 1

Preparation of the dye of Formula (6)



(6)

(a) Monoazo stage



5-Amino-2-(4'-methylpiperazino)benzoic acid (23.5g) was added to water (400ml) and conc HCl (30ml) added. $NaNO_2$ (6.9g) was added at 0-10°C and the mixture stirred at 0-10°C for 1 hour. Excess HNO_2 was removed from the diazo solution by addition of a little sulphamic acid.

An approximately 50/50 mixture of 5-amino-2-naphthoic acid and 8-amino-2-naphthoic acid (18.7g) was added to water (200ml) and the pH adjusted to 9.0 by addition of 2N NaOH solution. This solution was added to the above diazo solution at 0-10°C and the mixture stirred for 18 hours allowing the temperature to rise to 20°C.

The monoazo dye was filtered off, washed with 10% NaCl solution and dried at 60°C.

(b) Disazo stage

The monoazo dye (18.9g) from Stage (a) was added to water (400ml) and conc HCl (10ml) added. $NaNO_2$ (2.0g) was added at 0-10°C

and the mixture stirred for 1 hour at 0-10°C. Excess HNO_2 was removed form the diazo solution by addition of a little sulphamic acid.

Gamma acid (8.0g) was dissolved in water (300ml) by addition of 2N sodium hydroxide solution to pH 10. Na_2CO_3 (10.0g) was added and the above diazo solution was added at 0-10°C maintaining the pH at 10 by addition of 2N NaOH solution. The mixture was then stirred for 18 hours allowing the temperature to rise to 20°C.

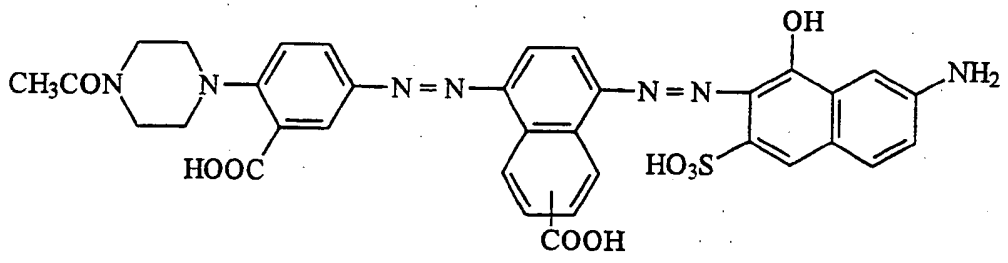
The solution was screened to remove a small amount of insoluble matter and the pH adjusted to 5 by addition of conc HCl. The precipitated product was filtered off, and washed with 10% NaCl solution. The filter paste was dissolved in water (300ml) and the solution added to a 1N HCl (500ml) to precipitate the dye in its free acid form. This was filtered off and converted to the ammonium salt by adding to water (300ml) and adjusting the pH to 9.5 by addition of conc NH_4OH.

The solution was dialysed to remove Cl^- ions, screened through a 0.45μ filter, the solvent evaporated and the product dried at 60°C.

The product of Formula (6) in the form of the ammonium salt was made into an ink (2.5%) in 92.5:7.5 water:2-pyrrolidone. When printed onto plain paper using a thermal ink jet printer it gave strong black prints having good light fastness and high water fastness.

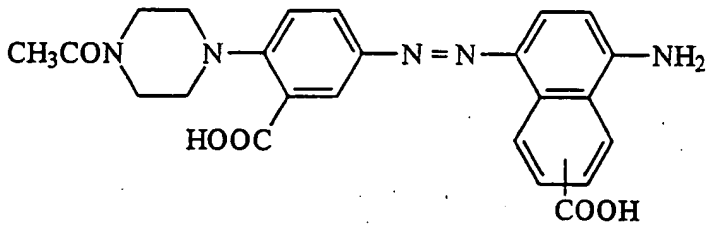
Example 2

Preparation of the dye of formula (7)



(7)

(a) Monoazo Stage (Formula (7a))



(7a)

In place of the 5-amino-2-(4'-methyl-piperazino) benzoic acid (23.5g) used in Example 1 Stage (a) there was used 5-amino-2-(4'-acetylpiperazino)benzoic acid (26.4g).

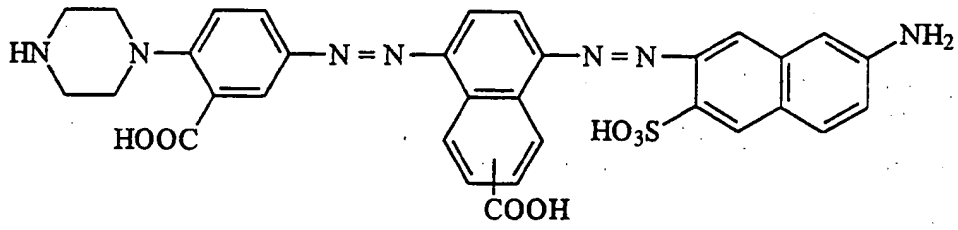
(b) Disazo Stage

In place of the monoazo product used in Example 1 (b) the monoazo product of Example 2 (a) was used.

The product of Formula (7) was converted to the dry ammonium salt by the method of Example 1. When made into an ink (3% in 90:10 water : diethyl glycol) and printed onto plain paper using a thermal ink jet printer it gave a strong black image with very high waterfastness and good light fastness.

Example 3

Preparation of the dye of formula (8)



(8)

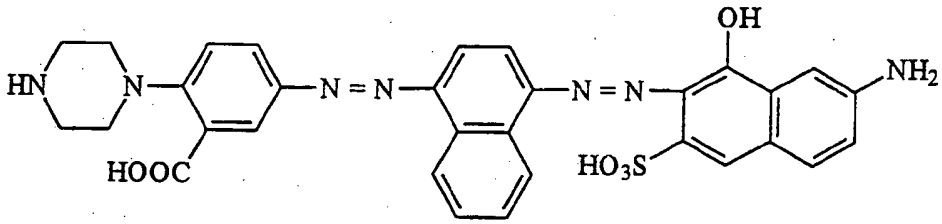
The product of Formula (7) as in Example 2 (10g) was added to 2N NaOH solution (400 ml) and stirred at 70-80°C for 3 hours. The pH was adjusted to 5 by addition of conc HCl and the mixture allowed to cool to 20°C. The precipitated product was filtered, washed with 10% NaCl solution and dried.

The product of Example (8) was converted to its dry ammonium salt as described in Example 1. When made into an ink (2.5% in water : diethylene glycol 90/10) and printed onto plain paper using a

thermal ink jet printer it gave a strong black image with excellent waterfastness and good light fastness.

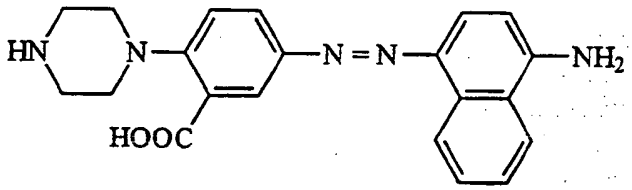
Example 4

Preparation of the dye of formula (9)



(9)

(a) Monoazo Stage (Formula (9a))

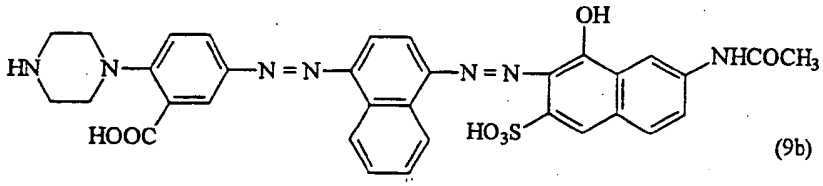


(9a)

5-Amino-2-piperazinobenzoic acid (18.0g) was added to a mixture of water (300 ml) and conc HCl (25 ml). $NaNO_2$ (5.6g) was added at 0-10°C and the mixture stirred at 0-10°C for 2 hours. Excess HNO_2 was removed from the resulting disazo solution by addition of a little sulphamic acid.

1-Naphthylamine (11.6g) was dissolved in ethanol (300 ml) and the solution added to the above disazo, the pH adjusted to 4 by addition of 2N NaOH solution and the mixture stirred for 18 hours. The pH was then adjusted to 5 with conc HCl and the precipitated product filtered, washed with a little water and dried.

(b) Disazo Stage (Formula (9b))



(9b)

The monoazo product prepared as in Example 4, Stage (a) (14.3g) was added to a mixture of water (300 ml) and conc HCl (10ml). $NaNO_2$ (1.8g) was added at 0-10°C and the mixture stirred at 0-10°C for 2 hours. Excess HNO_2 was removed from the resulting diazo solution by addition of a little sulphamic acid.

N-Acetyl-Gamma acid (15g) was dissolved in water (300ml) and the solution added to the above diazo solution. The pH was then adjusted to 7-8 and the mixture stirred for 18 hours after which the product was filtered and washed with 10% NaCl solution.

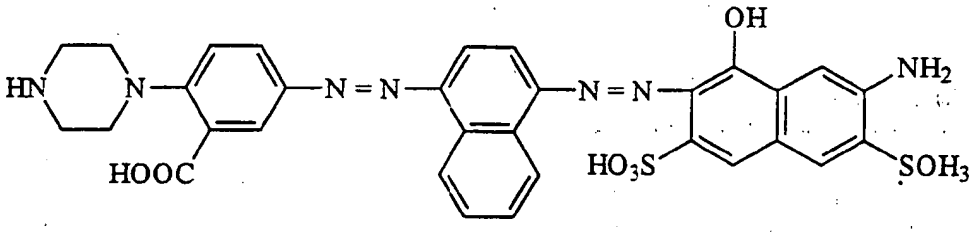
(c) Hydrolysis

The product obtained in Example 4, Stage (b) was added to 2N NaOH solution (800 ml) and stirred at 70-80°C for 3 hours. The pH was then adjusted to 7 by addition of conc HCl and the precipitated product filtered, washed with 10% NaCl solution and dried. It was converted to the dry ammonium salt as described in Example 1.

When made into an ink (2.5% in water:2-pyrrolidone 90:10) and printed onto plain paper using a thermal ink jet printer, the product of Formula (9) gave a black image having excellent water fastness and goof light fastness.

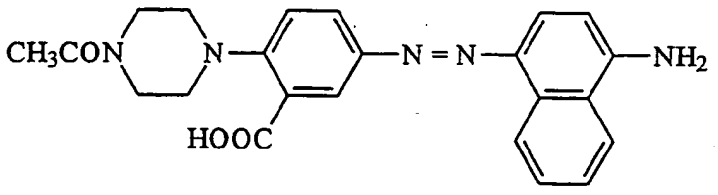
Example 5

Preparation of the dye of formula (10)



(10)

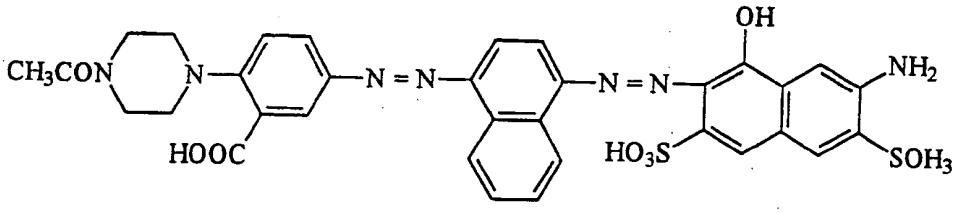
(a) Monoazo Stage (Formula 10a)



(10a)

In place of 5-amino-2-piperazinobenzoic acid (18.0g) used in Example 4, Stage (a), 5-amino-2-(4'-acetylpiperazino)benzoic acid (21.4g) was used.

(b) Disazo Stage



(10b)

In place of the monoazo product used in Example 4, Stage (b) the monoazo product prepared in Example 5, Stage (a) was used and in place of N-acetyl-Gamma acid used in Example 4, Stage (b) there was used 2R Acid (7-amino-1-hydroxy-3,6-disulphonic acid).

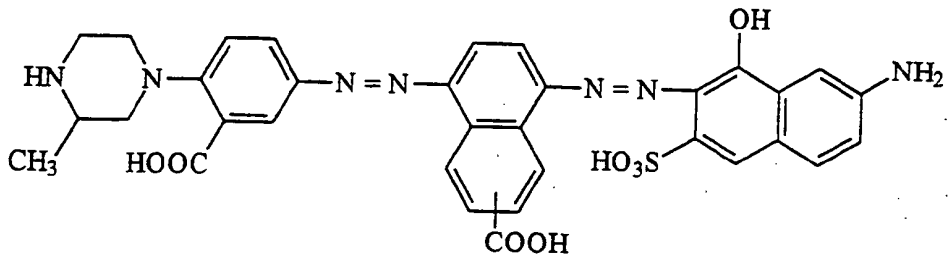
(c) Hydrolysis Stage

The method used in Example 4, Stage (c) was used except that in place of the disazo compound used in Example 4, Stage (c) there was used the disazo product prepared in Example 5, Stage (b).

It was converted to the dry ammonium salt as described in Example 1. When made into an ink (2.5% in water : 2-pyrrolidone, 90:10) and printed onto plain paper using a thermal ink jet printer it gave a black image with good waterfastness and high light fastness.

Example 6

Preparation of the dye of formula (11)



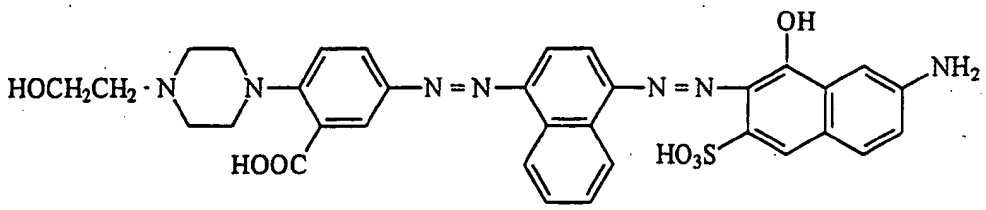
(11)

In place of the 5-amino-2-(4'-methyl-piperazino)benzoic acid used in Example 1 there may be used 5-amino-2-(3'-methyl-piperazino)benzoic acid. It may be converted to the dry ammonium salt by the method of Example 1. When made into an ink (2.5% in water : 2-

pyrrolidone 90:10) and printed onto plain paper using a thermal ink jet printer it will give a black image with high waterfastness and good light fastness.

Example 7

Preparation of the dye of formula (12)

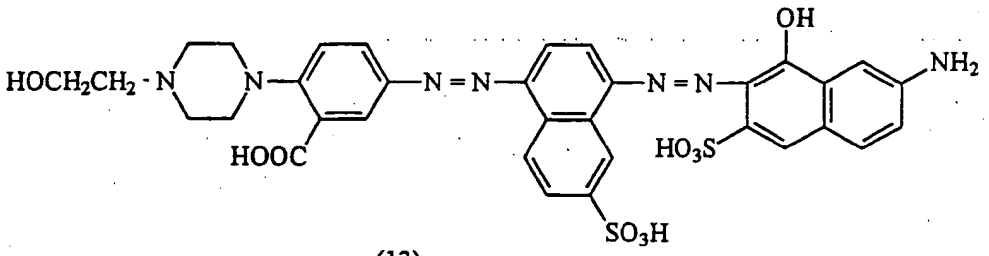


(12)

In place of the 5-amino-2-piperazino-benzoic acid used in Example 4 there may be used 5-amino-2-[4'-(2-hydroxyethyl) piperazino] benzoic acid. It may be converted to the dry ammonium salt by the method of Example 1. When made into an ink (2.5% in water : diethylene glycol, 90:10) and printed onto plain paper using a thermal ink jet printer it will give a black image with high waterfastness and good light fastness.

Example 8

Preparation of the dye of formula (13)

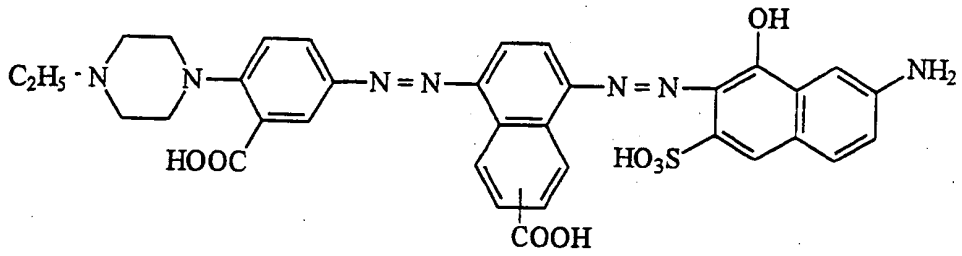


(13)

In place of the 1-naphthylamine used in Example 7, there may be used 1-naphthylamine-7-sulphonic acid. It may be converted to the dry ammonium salt by the method of Example 1. When made into an ink (2.5% in water : 2-pyrrolidone, 90:10) and printed onto plain paper using a thermal ink jet printer it will give a black image with high waterfastness and good light fastness.

Example 9

Preparation of the dye of formula (14)

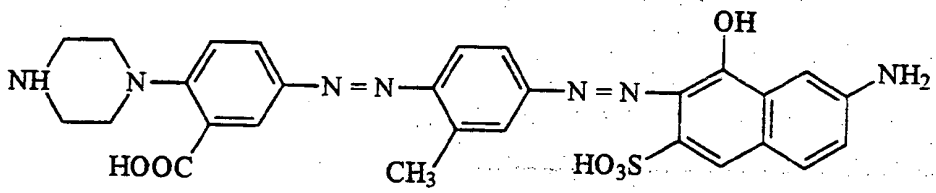


(14)

In place of 5-amino-2-(4'-methyl-piperazino)benzoic acid used in Example 1 there may be used 5-amino-2-(4'-ethylpiperazino)-benzoic acid. The product of Example (14) may be converted to the dry ammonium salt by the method of Example 1. When made into an ink (2.5% in water : 2-pyrrolidone, 90:10) it will give a black image with high waterfastness and good light fastness.

Example 10

Preparation of the dye of formula (15)

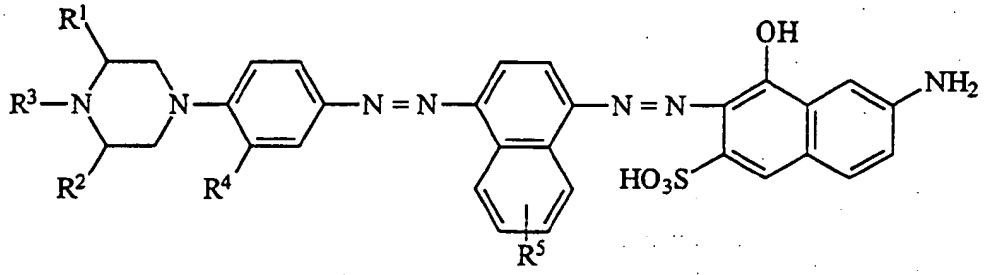


(15)

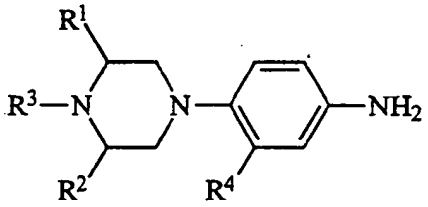
In place of 1-naphthylamine used in Example 4 there may be used 2-methoxy-5-methylaniline and the product of Example (15) may be converted to the dry ammonium salt by the method described in Example 1. When made into an ink (2.5% in water : 2-pyrrolidone, 90:10) it will give a black image with high waterfastness and good light fastness.

Each of the dyes of general Formulae 16 and 17 listed in Tables 1 and 2 may also be prepared by the method of Example 1 using an equivalent amount of an amine of Formula (18) or (19) respectively in place of the 5-amino-2-(4'-methylpiperazino)benzoic acid used in Example 1, Stage (a), an equivalent amount of the amine of Formula (20) or (21) respectively in place of the 50/50 mixture of 5-amino-2-naphthoic acid and 8-amino-2-naphthoic acid used in Example 1, Stage

(a) and an equivalent amount of the Gamma acid, or compound of Formula (22), respectively in place of the Gamma acid used in Example 1, Stage (b). When made into inks as the ammonium salts (2.5% in water : 2-pyrrolidone 90:10) each dye will give a black image having high waterfastness and good light fastness when printed onto plain paper using a thermal ink jet printer.



(16)



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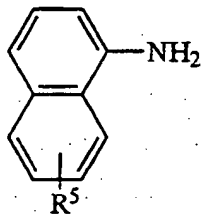
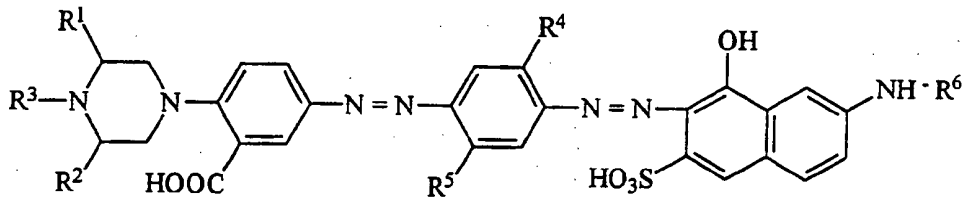


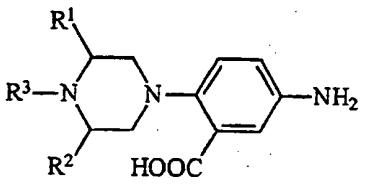
(20)

TABLE 1

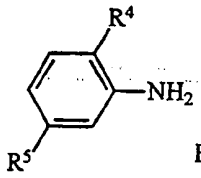
Example	R^1	R^2	R^3	R^4	R^5
11	H	H	C_2H_5OOC-	CO_2H	H
12	H	H	$HOOCCH_2$-	CO_2H	H
13	H	H	$HOC_2H_4OC_2H_4$-	CO_2H	H
14	H	H	$HOCH_2CH_2$-	H	CO_2H
15	H	H	$C_6H_5CH_2$-	CO_2H	CO_2H
16	CH_3	CH_3	H	CO_2H	CO_2H
17	H	H	H	SO_3H	CO_2H



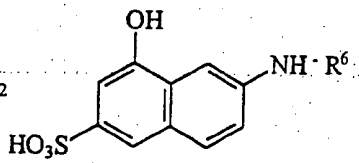
(17)



(19)



(21)



(22)

Table 2

Example	R^1	R^2	R^3	R^4	R^5	R^6
18	H	H	H	OCH_3	NH_2	H
19	H	H	CH_3	OCH_3	NH_2	H
20	H	H	$HOCH_2CH_2$	OCH_3	NH_2	H
21	H	H	H	OCH_3	OCH_3	C_6H_5
22	H	H	H	OCH_3	CH_3	CH_3
23	CH_3	H	H	OCH_3	NH_2	H
24	H	H	CH_3	OC_2H_5	OC_2H_5	H
26	H	H	CH_3	OC_2H_5	NH_2	H

Examples of other specific liquid media which can be used to prepare inks containing the dyes disclosed in Examples 1 to 26 and other dyes within the scope of the present invention are:

Water (60); Ethylene glycol (40)

Water (85); Diethylene glycol (15)

Water (90); Diethylene glycol (10)

Water (65); Glycerol (25); Triethanolamine (10)

Water (80); Ethylene glycol (15); Polyethylene glycol, MW 200 (5)

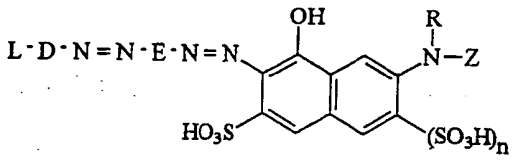
Water (80); Ethylene glycol (15); N-Methylpyrrolidone (5)

Water (80); Ethylene glycol (15); 2-Pyrrolidone (5)

Water (90); 2-Pyrrolidone (10)

CLAIMS

1. A compound of Formula (1) and salts thereof:

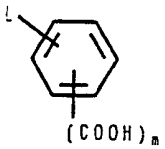


(1)

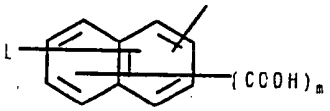
wherein:

- L is optionally substituted piperazinyl
- D is optionally substituted phenylene or naphthylene;
- E is optionally substituted phenylene, naphthylene or quinolinylene;
- R is H or C_{1-4}-alkyl;
- n has a value of 0 or 1; and
- Z is H, alkyl or aryl free from water-solubilising groups.

2. A compound according to Claim 1 wherein the group represented by L-D- is of the Formula (3):



(3)

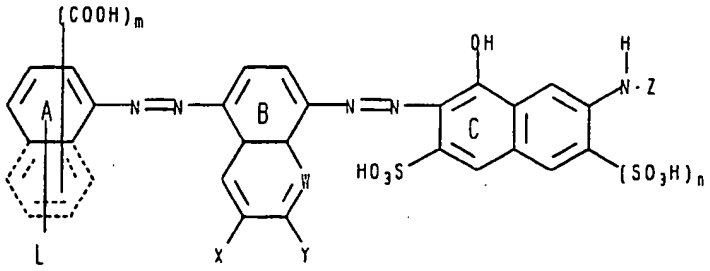


(4)

wherein

- m is 0 or 1; and
- L is of Formula (2) in which p is 0 or 1; V is CH_3 or OCH_3; and K is selected from H, C_{1-4}-alkyl; formyl; C_{1-4}-alkyl-carbonyl; phenylcarbonyl; C_{1-4}-alkoxycarbonyl; phenoxycarbonyl and hydroxy-C_{1-4}-alkyl.

3. A dye of Formula (5) and salts thereof:



(5)

wherein

n is 0 or 1;

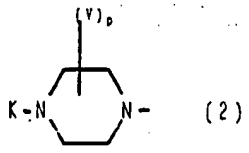
W is C-H, C-COOH or N;

X is H, COOH or SO_3H;

Y is H, COOH or SO_3H;

Z is H, aryl or substituted aryl free from water-solubilising groups; and

and L is of Formula (2):



(2)

wherein:

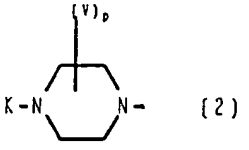
K is H or optionally substituted alkyl, aryl, acyl or ester;

V is optionally substituted alkyl; and

p is 0, 1 or 2.

provided that (1) at least one of X and Y is H or COOH and (2) W is C-H or N when X and Y are both COOH.

4. A compound according to any one of Claims 1 to 3 wherein L is of Formula (2):



(2)

wherein:

K is H or optionally substituted alkyl, aryl, acyl or ester;

V is optionally substituted alkyl; and

p is 0, 1 or 2.

5. A compound according to Claim 4 wherein the piperazinyl group is selected from piperazin-1-yl, 4-hydroxyethylpiperazin-1-yl,

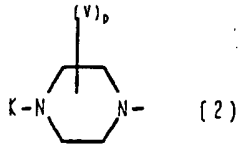
4-acetyl-piperazin-1-yl, 3-methylpiperazin-1-yl, 3-methyl-4-acetyl-piperazin-1-yl, 4-formylpiperazin-1-yl and 4-methylpiperazin-1-yl.

6. A compound according to any one of Claims 1 to 5 in the form of an ammonium or substituted ammonium salt.

7. A compound of the formula, L-D-NH_2, wherein

D is phen-1,4-ylene or 3-carboxyphen-1,4-ylene; and

L is of the Formula (2):



(2)

wherein:

K is H or optionally substituted alkyl, aryl, acyl or ester;

V is optionally substituted alkyl; and

p is 0, 1 or 2.

8. A compound selected from 3-Carboxy-4-piperazin-1-ylaniline, 4-(4'-acetylpiperazin-1-yl)-3-carboxyaniline, 3-carboxy-4-(3'-methyl-piperazin-1-yl)-aniline, 3-carboxy-2-(3'-methyl-4'-acetyl-piperazin-1-yl)-aniline and 4-(4'-[2-hydroxyethyl]-piperazin-1-yl)-aniline.

9. An ink comprising a compound according to any one of Claims 1 to 6 and a liquid medium.

10. A process for applying an image to a substrate comprising applying an ink according to Claim 9 to the substrate with an ink jet printer.

11 A substrate carrying an image comprising a compound according to any one of Claims 1 to 6.

INTERNATIONAL SEARCH REPORT

Intern· ·al Application No
PCT/GB 94/02637

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09B31/08 C09D11/00 D21H21/28 C07D295/14 C07D295/18
C07D295/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09B C09D C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 356 080 (IMPERIAL CHEMICAL INDUSTRIES PLC) 28 February 1990 cited in the application see claims; examples	1-12
X	FR,A,1 441 795 (GENERAL ANILINE AND FILM CORPORATION) 2 May 1966 see examples 5,1	8,9
X	EP,A,0 063 826 (DR. KARL THOMAE GMBH) 3 November 1982 see page 21, line 1 - line 2; line 5 - line 8; line 11 - line 12 see page 19, line 5 - line 6	8
X	EP,A,0 006 711 (JANSSEN PHARMACEUTICA N.V.) 9 January 1980 see page 39; example I	8

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
10 March 1995	10. 04. 95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Ginoux, C

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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